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FABRICATION OF Cu-BASED SiC COMPOSITES BY SPARK PLASMA SINTERING OF Cu-NITRATE COATED SiC POWDERS

An optimum route to fabricate the Cu-based SiC composites with homogeneous microstructure was investigated. Three methods for developing the densified composites with sound interface between Cu and SiC were compared on the basis of the resulting microstructures. Starting with three powder mixtures of elemental Cu and SiC, elemental Cu and PCS coated SiC or PCS and Cu-nitrate coated SiC was used to obtain Cu-based SiC composites. SEM analysis revealed that the composite fabricated by spark plasma sintering using elemental SiC and Cu powder mixture showed inhomogeneous microstructure. Conversely, dense microstructure with sound interface was observed in the sintered composites using powder mixture of pre-coated PCS and Cu-nitrate onto SiC. The relationship between powder processing and microstructure was discussed based on the role of coating layer for the wettability

Keywords: Cu-SiC composites, Cu-nitrate, Spark plasma sintering, Microstructure

1. Introduction

Cu with high thermal conductivity is promising candidate for application in electronic packaging and thermal management materials. However, the application field of this material is limited because of higher coefficient of thermal expansion (CTE) than the Si substrate in electronic packaging [1]. Recently, Cu-based composites with low CTE dispersoids have become focus for thermal management applications [2-4]. Among the potential dispersoid materials, SiC can be an attractive candidate due to its low CTE and high thermal conductivity [5,6]. Generally, method for the fabrication of Cu-based SiC composites involves powder metallurgy process as sintering of Cu and SiC powder compact. However, relatively poor thermal properties of Cu-based SiC composite were usually obtained because of the decomposition of Si in SiC and inhomogeneous microstructure by poor wettability between Cu and SiC [7]. Therefore, the key to achieving a useful Cu-based SiC composites for thermal management application is control of the interfacial reaction between Cu and SiC.

In this study, we attempt to fabricate the Cu composites dispersed with SiC particles by means of the spark plasma sintering using polycarbosilane (PCS) and Cu-nitrate coated SiC powders, in which PCS and Cu-nitrate were pyrolyzed and hydrogen-reduced for the formation of SiOC and Cu coating layer onto SiC powders, respectively. Moreover, we discuss the effect of the coating on the densification and microstructural characteristics of the sintered composites.

2. Experimental

Three different fabrication processes were applied to obtain the powder mixtures. The first one used mixture of ball-milled SiC with an average size of 20 μm and 70 vol% Cu metal powder with an average size of 30 mm. In the second process, PCS was used for pre-coating of SiOC onto SiC powder. Weighted PCS, corresponding to the thickness of about 100 nm on the SiC powder, was dissolved in hexane solution and mixed with SiC powder. The mixtures were cured and pyrolyzed at 1600°C. Then, Cu powder was mixed with the pyrolyzed powder and ball-milled for 10 h with high purity ZrO_2 balls. The detailed procedure is described elsewhere [8]. The third one used mixture of PCS-coated SiC and Cu-nitrate as source material for Cu. The mixtures were initially calcined at 300°C in air and hydrogen-reduced at 350°C for 1 h to obtain Cu-coated SiC powders. Subsequently, Cu metal powder was mixed with the above-mentioned mixtures by ball milling.

The densification of the powder mixtures was carried out using spark plasma sintering with a heating rate of 100°C/min at 700°C for 10 min in vacuum under an applied pressure of 30 MPa. The processed powders and composites were characterized by X-ray diffraction (XRD, D/Max-IIIC, Rigaku Denki Co., Japan) analysis. The microstructure and elemental analysis were observed by scanning electron microscopy (SEM, JSM-6700F, JEOL Co., Japan) equipped with an energy dispersive X-ray spectroscopy (EDX).

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3. Results and discussion

Typical morphologies for the powder mixture and sintered composite are shown in Fig. 1. It is observed from Fig. 1a that rectangular SiC and spherical Cu powders mixed by ball milling for 10 h. To densify the powder mixture, spark plasma sintering at 700°C for 10 min was applied. As clearly seen from Fig. 1b, the SiC particles were mainly distributed in grain boundaries and many pores were observed. This inhomogeneous microstructure may be attributed to poor wettability between Cu and SiC, as described in the literature [7].

Figure 2 shows SEM micrograph of the sintered composite prepared from the mixture of Cu and PCS-coated SiC powders. Compared with the microstructure of Fig. 1b, homogeneous dispersion of SiC particles and dense microstructure were observed in the sintered composite. This change in microstructure was thought to be due to the improvement of wettability between SiC and Cu by PCS coating onto SiC powders which induced enhanced densification with homogeneous microstructure [8,9]. However, some pores and cracks between Cu and SiC particles are still in the sintered composite. Thus, the uniform pre-coating of Cu on SiC particles applied to developing the composite with sound interface.

In order to fabricate the SiC powders with homogeneously coated Cu particles on their surfaces, the powder mixture of PCS-SiC and Cu-nitrate was calcined at 300°C and hydrogen-reduced at 350°C for 1 h. The diffraction peaks from the calcined powder can be indexed as a-SiC and CuO phase as shown in Fig. 3a, whereas those form the hydrogen-reduced were composed entirely of a-SiC and Cu phase (Fig. 3b). This reduction behavior of CuO coincides with the reported work [10]. Typical SEM image for hydrogen-reduced powder is shown in Fig. 4, in which the Cu particles appears light and the SiC grey. It is clearly represented that fine Cu particles are homogeneously distributed on the surface of SiC particles. To fabricate SiC-70 vol% Cu composites, Cu metal powder was mixed with the hydrogen-reduced powders and sintered at 700°C and 30 MPa by spark plasma sintering.

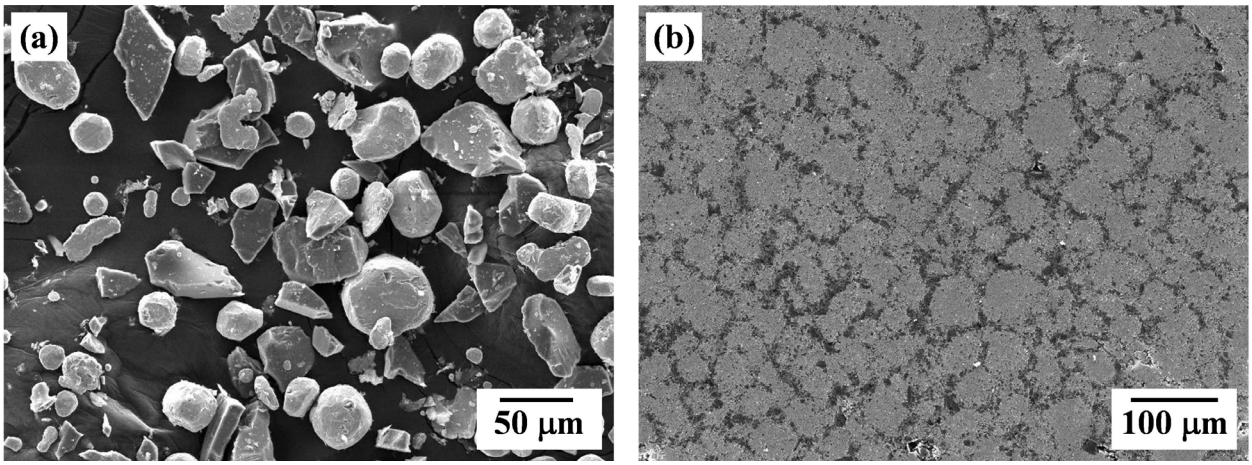

Fig. 1. SEM images of (a) ball-milled powder mixture of elemental Cu and SiC and (b) densified composite by spark plasma sintering at 700°C for 10 min

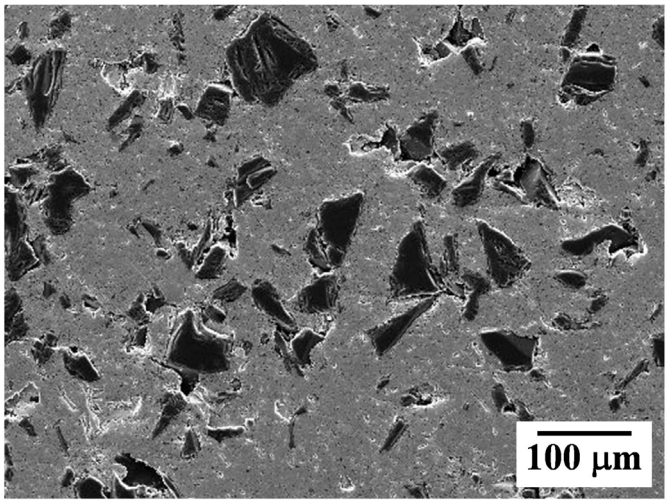

Fig. 2. Typical microstructure of sintered composite, prepared from Cu and PCS-coated SiC powders

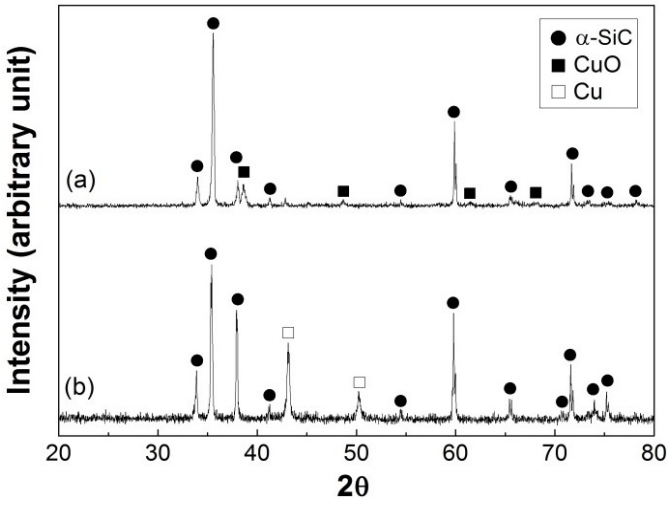

Fig. 3. XRD profiles for the powder mixtures of PCS and Cu-nitrate coated SiC at different stages of processing; (a) after calcination in air at 300°C for 2 h and (b) after hydrogen reduction at 350°C for 1 h

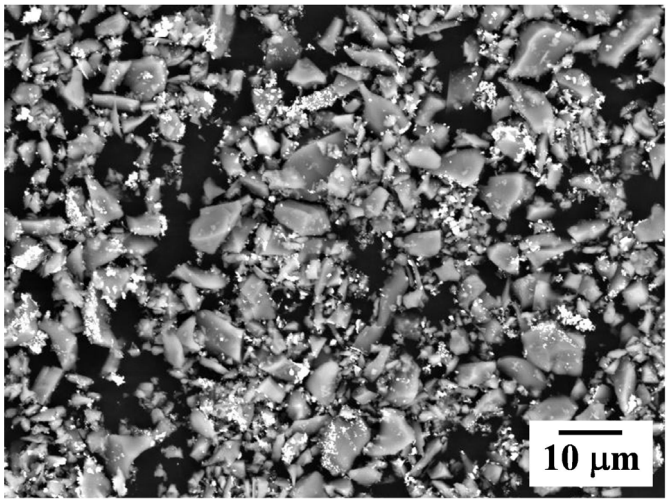

Fig. 4. Fine Cu particles coated SiC powders prepared by calcination and hydrogen reduction of Cu-nitrate

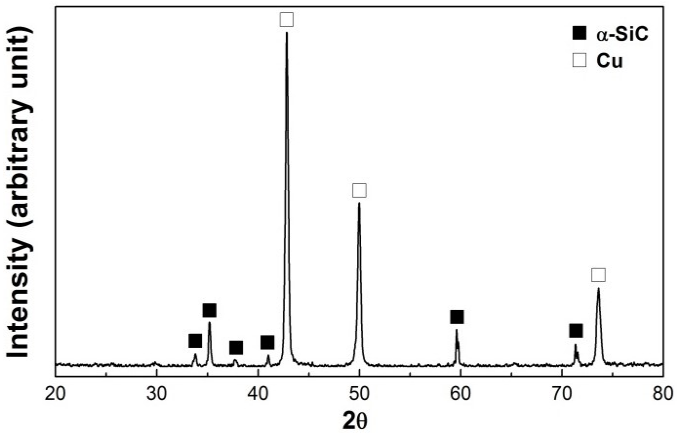

Fig. 5. XRD pattern of the Cu-30 vol% SiC composite, sintered for 10 min at 700°C using powder mixture of PCS and Cu-nitrate coated SiC mixed with elemental Cu

The XRD analysis shown in Fig. 5 revealed that the observed peaks in sintered specimen were registered as a-SiC and Cu phase without any reaction phase in the region of its resolution. As clearly seen from Fig. 6, the sintered composite using powder mixture with Cu-coated SiC showed relatively dense and homogeneous compared with that prepared by non-coated SiC powder (Fig. 2). For further characterization of sintered microstructure, SEM-EDX analysis was performed. As shown in Fig. 7, the sound interface between SiC and Cu phases was observed. Considering the role of coating phase in the wetting of SiC by Cu [11], therefore, it is suggested that the use of PCS and Cu-nitrate coated SiC powders is one of useful approaches to fabricate the dense composite with sound microstructure.

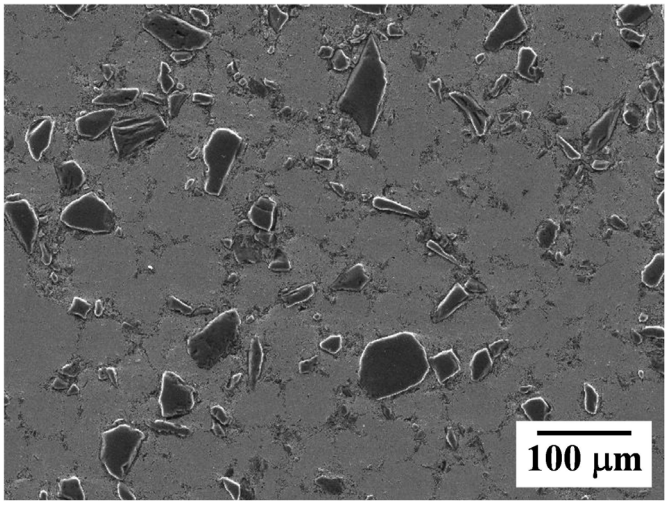

Fig. 6. SEM image of sintered composite, prepared from PCS and Cu-nitrate coated SiC mixed with elemental Cu powders

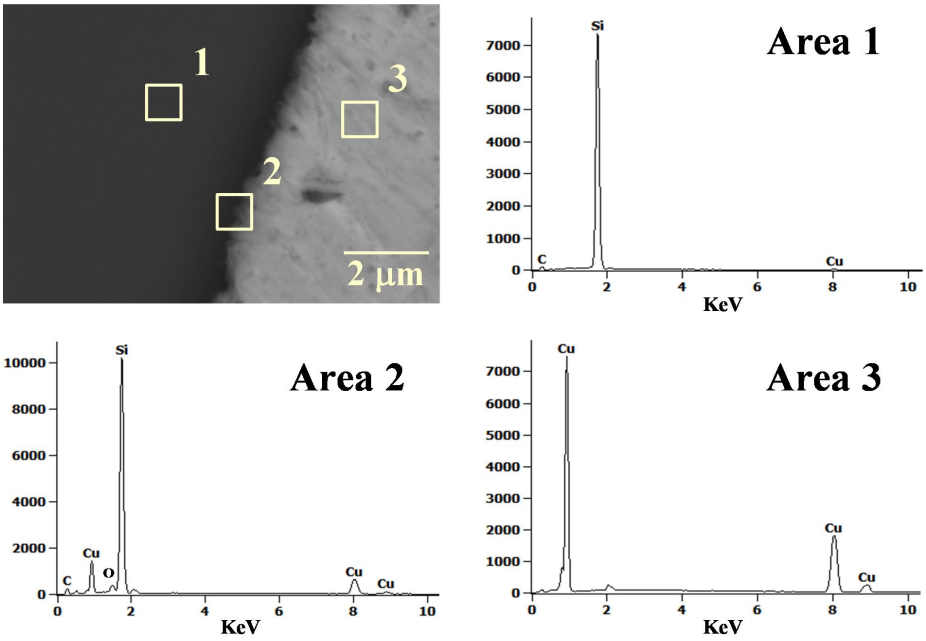

Fig. 7. Magnified image of the interface in Fig. 6 and EDX analysis for different areas

4. Conclusions

Three methods for the preparation of initial powder mixture for fabrication of Cu-based SiC composite have been presented and discussed on the basis of microstructural features. Cu-30 vol% SiC composite fabricated by the spark plasma sintering using Cu and PCS-coated SiC powder mixture showed dense and homogeneous microstructure compared with that using Cu and SiC powder mixture. In case of the sintered composite prepared by PCS and Cu-nitrate coated SiC powder mixture, more homogeneous microstructure with sound interface between Cu and SiC phase was observed. This change in microstructure was explained by the improvement of wettability between SiC and Cu by the coating layer. These results suggest that PCS and Cu-nitrate coating on SiC and further mixing of Cu powders as well as spark plasma sintering can provide the fabrication of the Cu-based SiC composite with homogeneous microstructure.

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